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(54) Flame retardant semiconductor encapsulating epoxy resin compositions

(57) Semiconductor encapsulating epoxy resin compositions comprising an epoxy resin, a phenolic resin curing agent, a fire retardant comprising zinc molybdate carried on spherical silica having a mean particle diameter of 0.2-20 μm and a specific surface of 1-20m²/g, and an inorganic filler are able to provide cured products having excellent fire retardance. The compositions have good flow and curing properties and excellent reliability and do not pose a hazard to human health or the environment.

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Description

BACKGROUND

[0001] The present invention relates to epoxy resin compositions of the kind suitable for encapsulating, with a particular view to providing cured products having fire retardance and freedom from the toxic substance antimony trioxide. The invention also relates to the preparation of such compositions, their use for semiconductor encapsulation and to semiconductor devices encapsulated with these compositions.

[0002] The semiconductor devices in use today are predominantly resin encapsulated diodes, transistors, integrated circuit (IC) chips, large scale integration (LSI) chips, and very large scale integration (VLSI) chips. Resin encapsulation is generally carried out with epoxy resin compositions because epoxy resins offer superior properties, (e.g., moldability, adhesion, electrical characteristics, mechanical characteristics, moisture resistance) compared with other thermosetting resins. Since semiconductor devices are used in all areas of our daily lives, including household appliances and computers, semiconductor encapsulants are required to be fire-retarding in the event that a fire occurs.

[0003] Halogenated epoxy resins and antimony trioxide (Sb_2O_3) are customarily included in epoxy resin compositions to increase the fire retardance. This combination of a halogenated epoxy resin with antimony trioxide has large radical-trapping and air-shielding effects in the vapor phase, thus conferring a high fire-retarding effect. However, halogenated epoxy resins generate noxious gases during combustion, and antimony trioxide has powder toxicity. Given their negative impact on human health and the environment, it would be desirable to entirely or substantially avoid these fire retardants.

[0004] Not only are resin compositions containing halogenated epoxy resins and antimony trioxide harmful to man and the environment, semiconductor devices encapsulated with these resin compositions have an inferior reliability when exposed to heat and moisture. This poor reliability arises because intermetallic compounds form at the junctions between aluminum electrodes and gold wire on the semiconductor device, causing an increase in electrical resistance and resulting also in wire breaks. The presence of the Br^- or Sb^+ ions within the resin composition as part of the fire retardant is known to promote the formation of the intermetallic compounds.

[0005] In view of the above, studies have been conducted on the use of hydroxides such as $Al(OH)_3$ and $Mg(OH)_2$ or phosphorus-containing fire retardants in place of halogenated epoxy resins and antimony trioxide. Unfortunately, because of various problems associated with the use of these alternative compounds, such as inferior curability of the resin composition during molding and poor moisture resistance in the cured product, they are not yet ready for practical application.

[0006] The object herein is to provide new and useful fire retardant epoxy resin compositions suitable for encapsulating semiconductor devices, as well as preparations and uses thereof, enabling the above-mentioned disadvantageous halogenated resins and antimony trioxide to be avoided.

[0007] Accordingly, this invention provides semiconductor encapsulating epoxy resin compositions comprising (A) an epoxy resin, (B) a phenolic resin curing agent, (C) a fire retardant comprising zinc molybdate carried on spherical silica having a mean particle diameter of 0.2 to 20 μm and a specific surface of 1 to 20 m^2/g, and (D) an inorganic filler. We find that such compositions provide cured products having a high fire retardance and excellent reliability, even containing no halogenated epoxy resin or antimony trioxide.

[0008] The epoxy resin used as component (A) in this invention may be any epoxy resin having at least two epoxy groups per molecule. Illustrative examples of suitable epoxy resins include novolac-type epoxy resins such as phenolic novolac epoxy resins and cresol novolac epoxy resins, triphenolalkane epoxy resins, aralkyl epoxy resins, biphenyl skeleton-containing aralkyl epoxy resins, biphenyl epoxy resins, heterocyclic epoxy resins, naphthalene ring-containing epoxy resins, bisphenol-type epoxy resins such as bisphenol A epoxy compounds and bisphenol F epoxy compounds, and stilbene epoxy resins. Any one or combination of two or more of these epoxy resins may be employed. Halogenated resins are preferably avoided.

[0009] No particular limit is imposed on the phenolic resin serving as curing agent (B) in the invention, so long as the phenolic resin has at least two phenolic hydroxyl groups in a molecule. Illustrative examples of typical phenolic resin curing agents include novolac-type phenolic resins such as phenolic novolac resins and cresol novolac resins, naphthalene ring-containing phenolic resins, triphenolalkane resins, aralkyl phenolic resins, biphenyl skeleton-containing aralkyl phenolic resins, biphenyl phenolic resins, alicyclic phenolic resins, heterocyclic phenolic resins, naphthalene ring-containing phenolic resins, and bisphenol-type phenolic resins such as bisphenol A and bisphenol F. Any one or combination of two or more of these phenolic resins may be employed.

[0010] The relative proportions of the epoxy resin (A) and the phenolic resin curing agent (B) used in the epoxy resin compositions are not subject to any particular limits, although it is preferred that the amount of phenolic hydroxyl groups in the curing agent (B) be from 0.5 to 1.5 moles, and especially 0.8 to 1.2 moles, per mole of epoxy groups in the epoxy resin (A).

The semiconductor encapsulating epoxy resin compositions therefore need not contain conventional fire retardants

such as antimony trioxide and brominated or otherwise halogenated epoxy resins. Instead, the inventive compositions use as the fire retardant (C) a substance prepared by supporting zinc molybdate on spherical silica having a mean particle diameter of 0.2 to 20 μm and a specific surface of 1 to 20 m^2/g. Zinc molybdate by itself is known to have a smoke-reducing and charring effect in burning plastic, but it exists in the form of very fine particles and so cannot easily be dispersed in a resin composition. However, by supporting zinc molybdate on spherical silica having a mean particle diameter of 0.2 to 20 μm and a specific surface of 1 to 20 m^2/g, there is obtained a fire retardant which is well dispersible in resin compositions. This fire retardant does not cause any loss in flow or curability during molding, and makes it possible to obtain epoxy resin compositions having sufficient fire retardance and excellent reliability in the cured state without using a halogenated epoxy resin or antimony trioxide.

[0011] The shape, particle diameter, and distribution of the supporting filler (spherical silica) are crucial for achieving fire retardance using as little zinc molybdate as possible, and for maintaining or enhancing the moldability of the epoxy resin composition.

[0012] Therefore, the spherical silica used as the zinc molybdate carrier should have a mean particle diameter of 0.2 to 20 pm, and preferably 0.3 to 10 pm. One of several ways in which the mean particle diameter can be determined is as the weight average value (median diameter) using a particle size distribution measurement apparatus based on the laser light diffraction technique . Particles with a mean particle diameter smaller than 0.2 μm are less dispersible within the resin compositions. A mean particle diameter greater than 20 pm discourages uniform dispersion and support of the zinc molybdate, lowering the fire retardance. This in turn necessitates the use of a larger amount of the fire retardant, which is economically undesirable. The specific surface, as obtained by a suitable technique such as BET adsorption, is from 1 to 20 m^2/g, and preferably from 2 to 18 m^2/g. Particles with a specific surface of less than 1 m^2/g retard the uniform support of zinc molybdate, resulting in a lower fire retardance. On the other hand, at a specific surface above 20 m^2/g, dispersibility within the resin composition declines.

[0013] The zinc molybdate and the spherical silica serving as the carrier are used in relative proportions such that the content of zinc molybdate based on the total of this fire retardant (i.e., the total amount of zinc molybdate and the spherical silica serving as the carrier) is preferably 1 to 50% by weight, and more preferably 5 to 40% by weight. A zinc molybdate content of less than 1% by weight may be insufficient to achieve sufficient fire retardance, whereas a content greater than 50% by weight may make uniform support of the zinc molybdate on the spherical silica difficult to achieve.

[0014] The amount of fire retardant (i.e., the total amount of zinc molybdate and the spherical silica serving as the carrier) in the epoxy resin compositions of the invention is preferably 1 to 300 parts by weight, more preferably 3 to 200 parts by weight, and most preferably 5 to 100 parts by weight, per 100 parts by weight of the epoxy resin and the phenolic resin curing agent combined. Less than 1 part by weight of the fire retardant may fail to achieve a sufficient fire-retarding, whereas the use of more than 300 parts by weight may adversely affect the flow and curability of the composition during molding.

[0015] The zinc molybdate content within the fire retardant (i.e., the total amount of zinc molybdate and the spherical silica serving as the carrier) is preferably 0.02 to 35 parts by weight, more preferably 0.1 to 30 parts by weight, and most preferably 0.5 to 25 parts by weight, per 100 parts by weight of the epoxy resin and the phenolic resin curing agent combined. Less than 0.02 part by weight of zinc molybdate would fail to achieve a sufficient fire-retarding effect, whereas the inclusion of more than 35 parts by weight would lower the flow and curability of the composition during molding.

[0016] Within the fire retardant used herein, the uranium content is preferably not more than 10 ppb. At a uranium content higher than 10 ppb, the uranium content in the resulting epoxy resin composition becomes high enough for soft errors caused by a rays to arise in the semiconductor device when the composition is used as a memory chip encapsulant. To ensure that the fire retardant has a uranium content no higher than 10 ppb, a low α ray-grade spherical silica having a uranium content of less than 1 ppb is preferable for supporting the zinc molybdate.

[0017] The fire retardant used herein is an extremely effective fire retardant which has not been found to have a powder toxicity like that of antimony trioxide. Examples of commercial products that may be used as this fire retardant include Kemgard series such as Kemgard 1260, 1261, 1270, and 1271, all available from Sherwin-Williams Co.

[0018] The inorganic filler (D) included in the epoxy resin compositions of the invention may be any suitable inorganic filler other than component (C), e.g as commonly used in epoxy resin compositions. Illustrative examples include silicas such as fused silica and crystalline silica, alumina, silicon nitride, aluminum nitride, boron nitride, titanium oxide, and glass fibers. No particular limit is imposed on the mean particle diameter and shape of these inorganic fillers, although the use of spherical fused silica having a mean particle diameter of 5 to 40 μm is preferred because it endows the epoxy resin composition with good molding and flow characteristics.

[0019] The epoxy resin compositions preferably have inorganic filler loadings of preferably 400 to 1,200 parts, more preferably 450 to 1,000 parts by weight per 100 parts by weight of the epoxy resin and the phenolic resin curing agent combined. At less than 400 parts by weight, the epoxy resin combination may have a larger coefficient of expansion, resulting in greater stress on the semiconductor device and a decline in the device characteristics. Moreover, the

proportion of resin relative to the overall composition becomes larger, sometimes reducing the fire retardance that is a central requirement. On the other hand, more than 1,200 parts by weight of the inorganic filler may result in an excessive rise in viscosity during moulding, and thus a poor moldability. The content of inorganic filler within the epoxy resin composition (excluding the above-described fire retardant (C)) is preferably 55 to 92% by weight, and especially 57 to 90% by weight.

[0020] The inorganic filler used herein is preferably surface treated beforehand with a coupling agent such as a silane coupling agent or a titanate coupling agent in order to increase the bonding strength between the resin and the inorganic filler. Preferred examples of such coupling agents include epoxy group-containing silanes such as γ-glycidoxy-propyltrimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane; amino group-containing silanes such as N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane, γ-aminopropyltriethoxysilane, and N-phenyl-γ-aminopropyltrimethoxysilane; and mercaptosilanes such as γ-mercaptopropyltrimethoxysilane and γ-mercaptopropylmethyldimethoxysilane. No particular limitation is imposed on the amount of coupling agent used for surface treatment or the method of surface treatment.

[0021] In the practice of this invention, use is preferably made of a curing accelerator to promote the curing reaction between the epoxy resin and the curing agent. The curing accelerator may be any suitable substance that promotes the curing reaction. Illustrative, non-limiting examples of curing accelerators that may be used include phosphorus compounds such as triphenylphosphine, tributylphosphine, tri(p-methylphenyl)phosphine, tri(nonylphenyl)phosphine, triphenylphosphine triphenylborane, and tetraphenylphosphine tetraphenylborate; tertiary amine compounds such as triethylamine, benzyldimethylamine, α-methylbenzyldimethylamine, and 1,8-diazabicyclo[5.4.0]undecene-7; and imidazole compounds such as 2-methylimidazole, 2-phenylimidazole, and 2-phenyl-4-methylimidazole.

[0022] The semiconductor encapsulating epoxy resin compositions of the invention may also include various additives, if necessary. Illustrative examples include stress-lowering additives such as thermoplastic resins, thermoplastic elastomers, synthetic organic rubbers, and silicones; waxes such as carnauba wax, higher fatty acids, and synthetic waxes; colorants such as carbon black; and halogen trapping agents.

[0023] The inventive epoxy resin compositions may be prepared by compounding the epoxy resin, curing agent, inorganic filler, and other components in predetermined proportions, thoroughly mixing these components together in a mixer or other appropriate apparatus, then melting and working the resulting mixture using hot rolls, a kneader, an extruder or the like. The worked mixture is then cooled and solidified, and subsequently milled to a suitable size so as to give a molding material.

[0024] The resulting epoxy resin compositions of the invention can be effectively used for encapsulating various types of semiconductor devices. The method of encapsulation most commonly used is low-pressure transfer molding. The epoxy resin composition of the invention is preferably molded at a temperature of about 150 to 180°C for a period of about 30 to 180 seconds, followed by postcuring at about 150 to 180°C for about 2 to 16 hours.

[0025] We have found that the epoxy resin compositions described herein cure into products which have an excellent fire retardance. By enabling freedom from halogenated epoxy resins and antimony trioxide, the epoxy resin compositions avoid adverse impact on human health or the environment. Moreover, these resin compositions have good flow and curing properties when molded, and provide excellent reliability in the cured state.

EXAMPLE

[0026] Examples of the invention and comparative examples are given below by way of illustration. All parts in the examples are by weight.

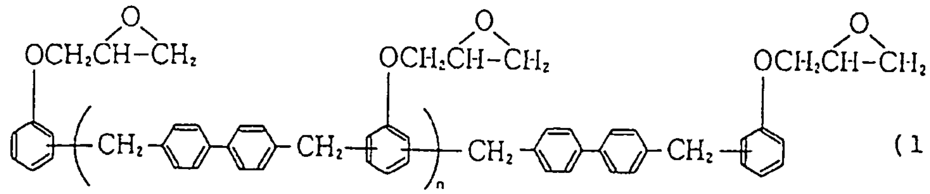
Examples 1 to 7, Comparative Examples 1 to 4

[0027] The respective combinations of components shown in Tables 1 and 2 were uniformly melted and worked a hot two-roll mill, then cooled and milled to give semiconductor encapsulating epoxy resin compositions. The following starting materials were used.

Epoxy Resins:

[0028]

(a) EOCN1020-55, an o-cresol novolac epoxy resin produced by Nippon Kayaku Co., Ltd. (epoxy equivalent, 200)
(b) YX40000HK, a biphenyl epoxy resin produced by Yuka Shell Epoxy (epoxy equivalent, 190)
(c) NC-3000P, an epoxy resin of formula (1) produced by Nippon Kayaku Co., Ltd. (epoxy equivalent, 272)



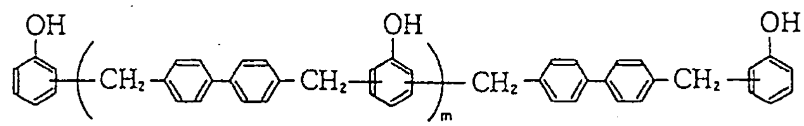
(1)

[0029] In the formula, n has an average value of 0.74.

Curing Agents:

[0030]

(d) DL-92, a phenolic novolac resin produced by Meiwa Kasei Industries, Ltd. (phenolic hydroxy equivalent, 110)
(e) MEH-7800SS, a phenolic aralkyl resin produced by Meiwa Kasei Industries, Ltd. (phenolic hydroxy equivalent, 175)
(f) MEH-7851L, a phenolic resin of formula (2) produced by Meiwa Kasei Industries, Ltd. (phenolic hydroxy equivalent, 199)



(2)

[0031] In the formula, m has an average value of 0.44.

Zinc Molybdate-Treated Silica:

[0032] Admafine LSO-25H (spherical silica with a mean particle diameter of 0.5 μm and a specific surface area by BET adsorption method of 14 m^2/g produced by Admatechs Co., Ltd.) treated with 19% by weight of zinc molybdate

Inorganic Filler:

[0033] Spherical fused silica produced by Tatsumori Ltd. (mean particle diameter, 20 μm)

Curing Accelerator:

[0034] Triphenylphosphine (Hokko Chemical Industry Co., Ltd.)

Parting Agent:

[0035] Carnauba wax (Nikko Fine Products, Ltd.)

Silane Coupling Agent:

[0036] KBM-403, a γ-glycidoxypropyltrimethoxysilane produced by Shin-Etsu Chemical Co., Ltd.
[0037] These compositions were measured for the following properties. The results are given in Tables 1 and 2.

(1) Spiral Flow:

[0038] Measured by molding at 175°C and 70 kgf/cm^2 for a molding time of 120 seconds using a mold in accordance with EMMI standards.

(2) Hardness When Molded:

[0039] Using the method described in JIS-K6911, a rod measuring 10×4×100 mm was molded at 175°C and 70 kgf/cm^2 for a time of 90 seconds. The hardness when hot was measured with a Barcol Impressor.

(3) Fire Retardance:

[0040] A 1.6mm (1/16") thick sheet was moulded and the fire retardance of the sheet was rated in accordance with UL 94 test specifications.

(4) Moisture Resistance:

[0041] A silicon chip measuring 6x6 mm on which aluminum wiring had been formed was adhesively bonded to a 14-pin dual in-line package (DIP) frame (Alloy 42), and the aluminum electrodes on the chip surface were wire bonded to the lead frame using 30 μm gold wire. The epoxy resin composition was then molded over the chip at 175°C and 70 kgf/cm^2 for a time of 120 seconds, and post-cured at 180°C for 4 hours. Twenty packages thus obtained were left to stand for 500 hours at 140°C and 85% relative humidity while being subjected to a bias voltage of 5V DC. The number of packages in which aluminum corrosion arose was counted.

Table 1

Ingredients (parts by weight)	Ex. 1	Ex. 2	Ex. 3	Ex.	4 Ex.	5 Ex.	6 Ex. 7
Epoxy resin (a)	64.6	64.6	--	--	--	--	--
Epoxy resin (b)	--	--	52.1	52.1	--	--	16.4
Epoxy resin (c)	--	--	--	--	57.8	57.8	38.4
Phenolic resin curing agent (d)	35.4	35.4	--	--	--	--	--
Phenolic resin curing agent (e)	--	--	47.9	47.9	--	--	--
Phenolic resin curing agent (f)	--	--	--	--	42.2	42.2	42.2
Inorganic filler	500	500	850	850	800	700	700
Curing accelerator	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Zinc molybdate-treated silica (zinc molybdate content, pbw)	100 (19)	5 (0.95)	100 (19)	5 (0.95)	1 (0.19)	5 (0.95)	5 (0.95)
Zinc molybdate	--	--	--	--	--	--	--
Aluminum hydroxide	--	--	--	--	--	--	--
Antimony trioxide	--	--	--	--	--	--	--
Brominated epoxy resin	--	--	--	--	--	--	--
Parting agent	3	3	3	3	3	3	3
Carbon black	2	2	2	2	2	2	2
Silane coupling agent	1	1	1	1	1	1	1
Properties							
Spiral flow (cm)	100	100	120	120	80	90	100
Hardness when molded	80	80	85	85	80	80	75
Fire retardance	V-0	V-0	V-0	V-0	V-0	V-0	V-0
Moisture resistance	0/20	0/20	0/20	0/20	0/20	0/20	0/20

Table 2

Ingredients (parts by weight)	CE 1	CE 2	CE 3	CE 4
Epoxy resin (a)	64.6	--	--	--
Epoxy resin (b)	--	--	52.1	52.1
Epoxy resin (c)	--	57.8	--	--
Phenolic resin curing agent (d)	35.4	--	--	--
Phenolic resin curing agent (e)	--	--	47.9	47.9
Phenolic resin curing agent (f)	--	42.2	--	--
Inorganic filler	500	800	850	850
Curing accelerator	1.2	1.2	1.2	1.2
Zinc molybdate-treated silica (zinc molybdate content, pbw)	-- (--)	-- (--)	-- (--)	-- (--)
Zinc molybdate	--	0.95	--	--
Aluminum hydroxide	--	--	--	50
Antimony trioxide	--	--	4	--
Brominated epoxy resin	--	--	6.2	--
Parting agent	3	3	3	3
Carbon black	2	2	2	2
Silane coupling agent	1	1	1	1
Properties				
Spiral flow (cm)	100	40	125	100
Hardness when molded	80	80	85	40
Fire retardance	burned	V-0	V-0	V-0
Moisture resistance	0/20	0/20	20/20	20/20

[0042] From Tables 1 and 2, it is apparent that the semiconductor encapsulating epoxy resin compositions of the examples were able to provide cured products which have excellent fire retardance. These compositions avoid ill effects on human health and the environment because they contain no halogenated epoxy resins or antimony trioxide. Moreover, these epoxy resin compositions have good flow and curing properties when molded, as well as excellent reliability. Semiconductor devices encapsulated with the epoxy resin compositions as described are fully fire retardant and highly reliable.

Examples 8 to 11, Comparative Examples 5 to 7

[0043] In these examples, spherical silica having different mean particle diameters and crushed silica obtained by milling were used as the zinc molybdate-supporting silica. Zinc molybdate was supported on these silicas in the concentrations shown in Table 3.

Table 3

Supporting silica	A	B	C	D	E	F
Mean particle size (μm)	1	5	15	30	0.5	0.1
Shape	spherical	spherical	spherical	spherical	crushed	spherical
Specific surface (m^2/g)	6	2.5	1.7	1.2	18	35
Concentration of zinc molybdate (%)	30	20	10	20	20	20

[0044] The zinc molybdate-treated silicas shown in Table 3 were compounded as the fire retardant with the other ingredients shown in Table 4. The ingredients in each case were uniformly melted and worked together in a hot two-roll mill, then cooled and milled to give semiconductor encapsulating epoxy resin compositions. The same starting materials as indicated above were used here to obtain these compositions.

Table 4

Ingredients (pbw)	Ex. 8	Ex. 9	Ex. 10	Ex. 11	CE 5	CE 6	CE 7
Epoxy resin (a)	64.6	--	64.6	--	64.6	64.6	--
Epoxy resin (b)	--	52.1	--	--	--	--	52.1
Epoxy resin (c)	--	--	--	57.8	--	--	--
Phenolic resin curing agent (d)	35.4	--	35.4	--	35.4	35.4	--
Phenolic resin curing agent (e)	--	47.9	--	--	--	--	47.9
Phenolic resin curing agent (f)	--	--	--	42.2	--	--	--
Inorganic filler	500	850	400	700	500	500	850
Curing accelerator	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Zinc molybdate-treated silica (A)	--	5	--	--	--	--	--
Zinc molybdate-treated silica (B)	70	--	--	--	--	--	--
Zinc molybdate-treated silica (C)	--	--	200	10	--	--	--
Zinc molybdate-treated silica (D)	--	--	--	--	100	--	--
Zinc molybdate-treated silica (E)	--	--	--	--	--	100	--
Zinc molybdate-treated silica (F)	--	--	--	--	--	--	5
Parting agent	3	3	3	3	3	3	3
Carbon black	2	2	2	2	2	2	2
Silane coupling agent	1	1	1	1	1	1	1
Properties							
Spiral flow (cm)	105	115	106	95	85	28	49
Hardness when molded	83	85	84	82	82	80	76
Fire retardance	V-0	V-0	V-0	V-0	burned	V-0	V-0
Moisture resistance	0/20	0/20	0/20	0/20	0/20	0/20	5/20

[0045] As can be seen from the results shown in Table 4, the silica with a mean particle diameter of 0.1 μm used in Comparative Example 7 had too large a surface area (or too small a mean particle size), resulting in poor wettability with the resin, poor flow by the composition, and poor moisture resistance in the cured product. In Comparative Example 6, the epoxy resin composition containing a large amount of crushed silica lacked flowability, resulting in poor molding properties. In Comparative Example 5, the use of spherical silica having a large mean particle diameter of 30 μm resulted in a lack of uniform dispersibility and poor fire retardance. Hence, it is apparent that semiconductor encapsulating epoxy resin compositions of good moldability and moisture resistance can be obtained by using as the fire retardant spherical silica having a mean particle diameter of 0.2 to 20 μm which has been treated with zinc molybdate.

[0046] Japanese Patent Application No. 132715/1998 is incorporated herein by reference.

[0047] Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described in the Examples.

Claims

1. Epoxy resin composition comprising:

(A) epoxy resin,
(B) phenolic resin curing agent,
(C) fire retardant comprising zinc molybdate carried on spherical silica having a mean particle diameter of 0.2 to 20 μm and a specific surface of 1 to 20m^2/g, and
(D) inorganic filler.

2. Epoxy resin composition of claim 1, wherein the fire retardant (C) is included in an amount of 1 to 300 parts by weight per 100 parts by weight of the epoxy resin (A) and the phenolic resin curing agent (B) combined.

3. Epoxy resin composition of claim 1 or claim 2 wherein the fire retardant (C) has a zinc molybdate content of 0.02 to 35 parts by weight per 100 parts by weight of the epoxy resin (A) and the phenolic resin curing agent (B) combined.

4. Epoxy resin composition according to any one of the preceding claims wherein the fire retardant (C) has a uranium content of not more than 10 ppb.

5. A method comprising the preparation of a composition according to any one of claims 1 to 4 by compounding said components thereof.

6. The use of a composition according to any one of claims 1 to 4 for semiconductor device encapsulation.

7. A semiconductor device encapsulated with an epoxy resin composition according to any one of claims 1 to 4 in a cured state.

Synopsis

Quaternary phosphonium compounds have been found to be extremely effective latent accelerators for anhydride-cured bisphenol A epoxy resins; at concentrations from 0.01% to 0.25%, fast gel times are found in the temperature range of 135°–200°C combined with very good storage properties at ambient temperatures. Using these materials as accelerators, it is possible to formulate long-life, one-component epoxy resins. From gel time data, Arrhenius plots were made for some of these phosphonium compounds, and results indicate low activation energy values of the order of 16.1 kcal/mole. Reaction mechanisms are proposed to explain the effectiveness of these phosphonium compounds as latent accelerators. The initiation mechanism probably involves the formation of hydrogen-bonded phosphonium–epoxy or phosphonium–anhydride complexes which rearrange on the application of heat to form activated species resulting in polymerization of the epoxy–anhydride components. The transfer of a proton from the phosphonium complex(es) to other epoxy or anhydride molecules would appear to be the rate-determining step in this initiation mechanism. Comparison of other well-known accelerators used for the anhydride cure of bisphenol A epoxy resins shows quaternary phosphonium compounds to be among the most effective accelerators disclosed to date.

INTRODUCTION

A considerable amount of effort has been devoted in recent years, mainly in the electrical industry, to develop a perfect latent catalyst for curing epoxy resins. This has been particularly the case in the manufacture of electrical equipment such as motors, transformers, and generators, where epoxy resins are utilized in such diverse processes as casting, potting, encapsulation, and vacuum-pressure impregnation (VPI). For reasons of economy and convenience, it is normal practice to store "one-package" epoxy resins (i.e., catalyzed resins) in large storage tanks in close proximity to the processing area. Thus, adequate catalyzed storage stability at ambient combined with efficient reactivity and cure at elevated temperatures are necessary prerequisites.

The specific properties required by an ideal "latent" catalyst would be the following: (a) It should give rapid cure of epoxy resins at moderately elevated temperatures (i.e., 120°–180°C). (b) It should be completely miscible with the resins at all temperatures. This is particularly true of impregnating resins. (c) The storage life of the catalyzed resin should be indefinite. In practice, the viscosity of the resin should not change appreciably at room temperature over periods ranging from several months to years. (d) It should not adversely affect the properties of the cured resin (e.g., tensile and electrical properties).

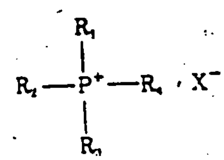
Numerous patents[1-3] have been issued in recent years on the development of latent catalysts for diglycidyl ether of bisphenol A resins (DGEBA), but most

fulfill only a few of the conditions outlined above. One of the most successful of these has been the boron trifluoride-monoethylamine complex[4] (BF_3-MEA) BF_3-400 (Harshaw Chemical Co. trademark). However, one of the serious disadvantages of this particular latent catalyst is the poor electrical properties at elevated temperatures of the epoxy resin in the cured state.[5]

To improve high-temperature stability over amine-cured systems and to give better physical and electrical properties above their heat distortion temperatures, it has been general practice in epoxy resin systems to use anhydride curing agents with DGEBA epoxy resins.[6] Most anhydride formulations require elevated-temperature cures with the ultimate properties dependent on postcures at temperatures of 150°C or higher.

For most commercial applications it is necessary to add some form of accelerator to the formulation to speed the rate of cure. Both acidic and basic accelerators can be used. Consequently, several latent accelerators have appeared on the commercial scene in recent years. Included among these are quaternary ammonium halides (such as benzyltrimethylammonium chloride[7]), stannous octoate,[3] zinc stearate,[8] "extra-coordinate" siliconate salts,[9] triethanolamine borate,[10] triethanolamine titanate,[11] and various other metal chelates.[12] However, all of these materials have been rejected for one reason or another, and the quest for improved latent accelerators for anhydride-cured epoxy resins has continued.

Recent work[13] in our laboratories has revealed a new family of latent accelerators. This new family of compounds is derived from the salts of tertiary organophosphines and aryl or alkyl halides which have the general structural formula



where R_1, R_2, R_3, and R_4 are alkyl or aryl groups and X^- is halogen, acetate, or dimethyl phosphate anion.

Most of the data reported here will be concerned with bisphenol A epoxy resin systems cured with the liquid anhydride 1-methyltetrahydrophthalic anhydride (the Union Carbide commercial designation for this material is ZZLA-0334). However, these quaternary phosphonium compounds have also been shown to be effective with other anhydrides such as hexahydrophthalic anhydride (HHPA).

EXPERIMENTAL

Seven different quaternary phosphonium salts were evaluated in this work: (i) methyltrioctylphosphonium dimethyl phosphate (MTOP-DMP), (ii) tetrabutylphosphonium acetate (TBPA), (iii) methyltributylphosphonium dimethyl phosphate (MTBP-DMP), (iv) benzyltriphenylphosphonium chloride (BTPPC), (v) tetrabutylphosphonium chloride (TBPC), (vi) methyltriphenylphosphonium dimethyl phosphate (MTPP-DMP), and (vii) triphenylethylphosphonium iodide (TPEPI).

With the exception of TPEPI, supplied by Arapahoe Chemical Company, Boulder, Colorado, all of the phosphonium compounds were supplied by Cincinnati Milacron, Reading, Ohio.

Most of the evaluation studies were made using a 1:1 stoichiometric bisphenol A epoxy–anhydride formulation. The various quaternary phosphonium compounds were added at a 0.01%–0.25% level (based on the combined anhydride and epoxy resin weights). With the exception of MTPP-DMP, which showed partial insolubility in the resin formulation, excellent solubilities at ambient temperature were found.

Gel Time Data

Initially, gel times were recorded on 10-g samples of resin in 2-in.-diameter aluminum dishes over the temperature range of 135°–170°C. Later, to give improved accuracy, the gel time measurements were made in 19 × 150 mm test tubes in a constant-temperature silicone oil bath using a Sunshine gel meter.

Storage Stability Data

Storage stability characteristics of the formulations were followed at room temperature (i.e., 25°C) using a Gardner–Holdt bubble viscometer (ASTM D154-56). Termination of a sample's catalyzed lifetime (i.e., storage life) was taken to be when the viscosity reached a value of 1000 cps at 25°C.

RESULTS

The data shown in Figures 1 and 2 indicate the effectiveness of two of the phosphonium compounds as accelerators for the epoxy–anhydride resin. Figure 1 gives "gel time" data as a function of temperature and accelerator concentration for the methyltrioctylphosphonium dimethylphosphate (MTOP-DMP) compound, whereas Figure 2 shows similar data obtained with tetrabutylphosphonium acetate (TBPA). It is noted that fast gel times (i.e., < 60 min) can be obtained with small amounts of accelerator (e.g., 0.06%), particularly at temperatures above 150°C. In the absence of accelerator the epoxy–anhydride resin shows very sluggish curing properties, the gel time at 150°C being in excess of 10 hr. In Figures 3–5, typical viscosity-versus-storage time curves are presented for the MTOP-DMP, MTBP-DMP, and TBPA phosphonium compounds, respectively. It is noted that "families" of curves can be constructed for each accelerator at their different concentrations. As might be anticipated, the viscosity changes become more rapid as the accelerator concentration increases.

However, appreciable latency is shown by these phosphonium compounds as demonstrated by the storage data shown in Table I. Using 1000 cps (at 25°C) as being the limiting viscosity, "storage lifetime" values can be assigned to each of the phosphonium compounds as indicated in Table I. It would appear that the nonhalide phosphonium compounds (e.g., MTOP-DMP and MTBP-DMP) exhibit higher latency than those containing halides. These differences may be linked to the presence of impurities or hydrolyzed byproducts in the halide compounds. In this respect it was noted that two of the materials investigated (i.e., BTPPC and TBPC) had pungent odors suggesting the presence of free organophosphine, presumably resulting from sample degradation or hydrolysis.

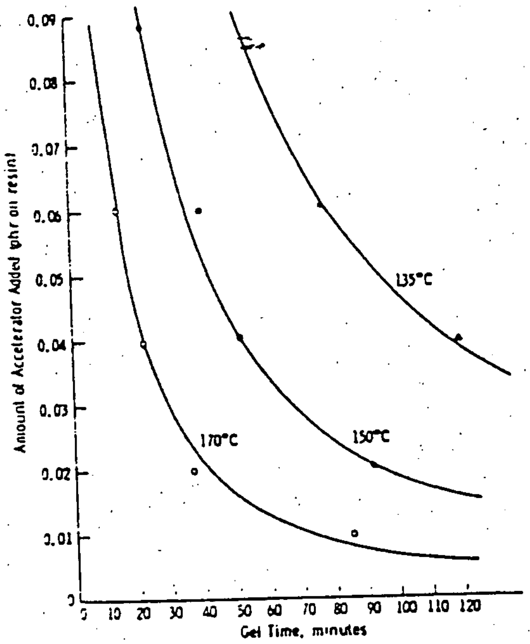


Fig. 1. Gel time data for epoxy–anhydride resin with MTOP-DMP accelerator (methyltrioctylphosphonium dimethyl phosphate).

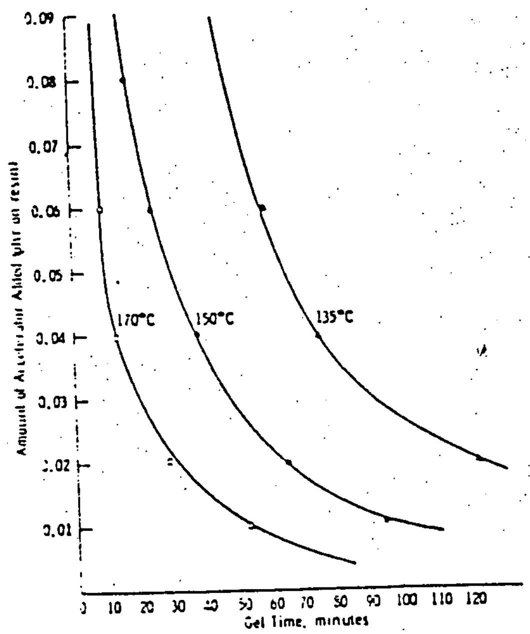


Fig. 2. Gel time data for epoxy–anhydride resin with TBPA accelerator (tetrabutylphosphonium acetate).

The three phosphonium compounds showing the best compromise between storage lifetime and catalytic effectiveness were MTOP-DMP, MTBP-DMP, and TBPA.

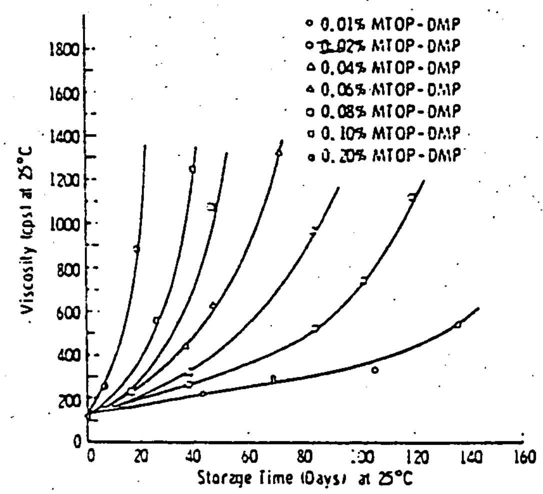


Fig. 3. Storage characteristics of epoxy-anhydride impregnant with different concentrations of MTOP-DMP (methyltrioctylphosphonium dimethyl phosphate).

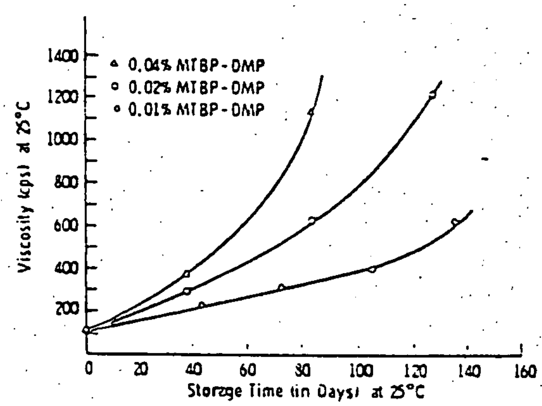


Fig. 4. Storage characteristics of epoxy-anhydride impregnant with different concentrations of MTBP-DMP (methyltributylphosphonium dimethyl phosphate).

In order to shed some light on the role of these quaternary phosphonium compounds in epoxy-anhydride systems, additional gel time data were obtained with the MTOP-DMP accelerator over the temperature range of 150°–200°C, using the constant-temperature bath and the Sunshine gel meter as mentioned previously. Relative reaction rate values could then be obtained at each temperature as shown in Table II for MTOP-DMP at a concentration of 0.04%.

In these calculations it was empirically assumed that the extent of reaction to the gel point was 50% so that the "relative reaction rate" is given by 50/gel time (in %/min).

This assumption may not be completely valid since the various crosslinking reactions in this resin system (e.g., etherification and esterification) may not vary uniformly with temperature (i.e., some crosslinks may be preferentially formed at the higher temperatures). However, this treatment does give an interesting insight into the role of quaternary phosphonium compounds in these systems. In Figure 6, an Arrhenius plot is shown for the data computed in Table II for the MTOP-DMP accelerator at 0.04% concentration. It is noted that a good linear

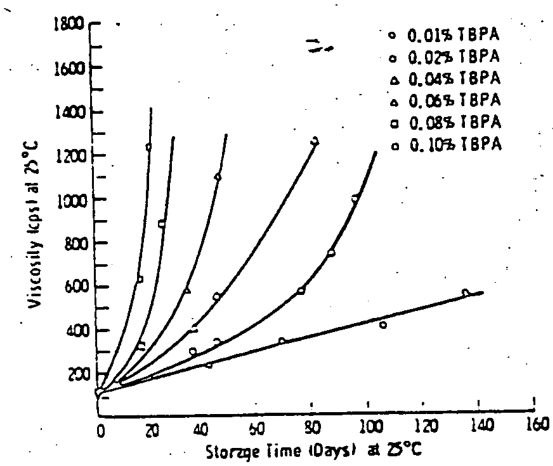


Fig. 5. Storage characteristics of epoxy-anhydride impregnant with different concentrations of TBPA (tetrabutylphosphonium acetate).

plot is obtained over the temperature range of 150°–200°C. From the slope of this plot an activation energy value of 16.1 kcal/mole is obtained.

This type of evaluation was then repeated for the MTOP-DMP and TBPA accelerators at higher concentrations in the resin (i.e., 0.25%). The gel time data

TABLE I
Storage Lifetime Data for the Quaternary Phosphonium Compounds with Epoxy-Anhydride Resin

Quaternary phosphonium compound used	Concentration in epoxy-anhydride resin, % w/w	Molar concentration, moles × 10^{-4} in 200 g resin	Storage lifetime at 25 °C,[a] days
Methyltrioctylphosphonium dimethyl phosphate (MTOP-DMP)	0.02	0.78	130
	0.04	1.56	85
	0.06	2.34	56
	0.10	3.90	45
Tetrabutylphosphonium acetate (TBPA)	0.02	1.06	112
	0.04	2.12	80
	0.06	3.18	42
	0.10	5.30	21
Methyltributylphosphonium dimethyl phosphate (MTBP-DMP)	0.01	0.59	160
	0.02	1.17	115
	0.04	2.34	85
Benzyltriphenylphosphonium chloride (BTPPC)	0.02	1.03	90
	0.10	5.15	28
Tetrabutylphosphonium chloride (TBPC)	0.02	1.36	90
	0.10	6.80	30
Methyltriphenylphosphonium dimethyl phosphate (MTPP-DMP)[b]	0.02	1.00	150
Triphenylethylphosphonium iodide (TPEPI)	0.02	0.96	85

[a] Number of days for viscosity to reach 1,000 cps at 25°C.
[b] Some insolubility in the resin detected with this material.

TABLE II
Relative Reaction Rates at Different Temperatures of Epoxy–Anhydride Resin with 0.04% Methyltrioctylphosphonium Dimethyl Phosphate

Temperature, °C	Gel times, min	Average value, min	Relative reaction Rate,[a] %/min
150	51.1	51.6	0.968
	52.1		
170	19.1	19.2	2.62
	19.2		
180	13.4	13.3	3.76
	13.2		
190	9.3	9.3	5.37
	9.3		
200	6.9	6.9	7.25
	6.9		

[a] Assuming 50% reaction to gel point ∴ relative reaction rate = 50%/gel time, min = x %/min

were used to compute relative reaction rates as before, and the Arrhenius plots for the two accelerators are given in Figure 7. This time, nonlinear plots were found over the temperature range of 150°–175°C for both MTOP-DMP and TBPA. The indication is that at the higher concentration of these accelerators, a change in the relative rates of the initiation and crosslinking reaction mechanisms occurs as a consequence of the phosphonium compound taking a direct role in the crosslinking processes.

It should be emphasized again that, although the treatment outlined above results in "activation energy" values, the use of data obtained in this way is questionable in view of the uncertainty of the assumption made in deriving these values.

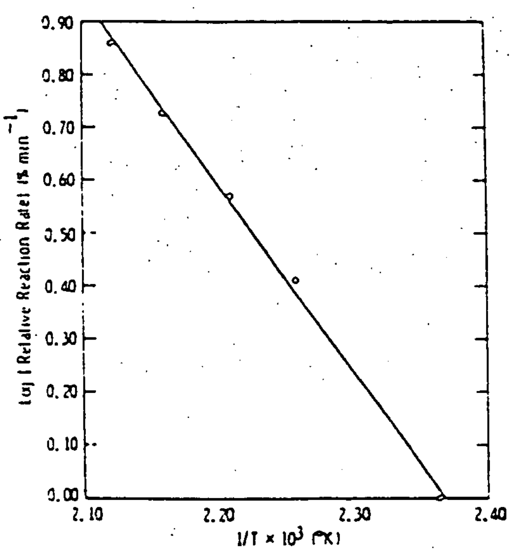


Fig. 6. Arrhenius plot for epoxy–anhydride resin gel time data (with 0.04% MTOP-DMP).

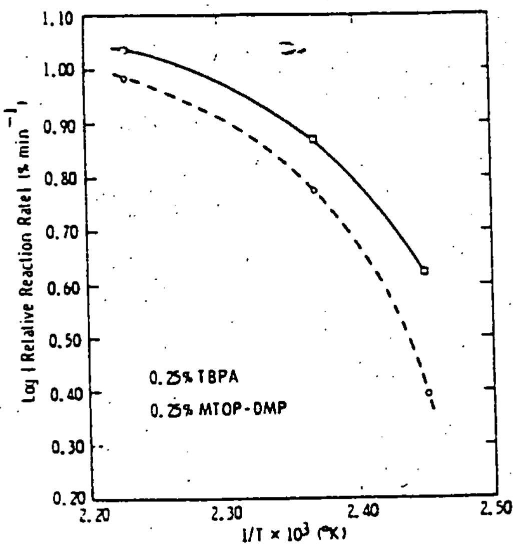


Fig. 7. Arrhenius plot for epoxy-anhydride resin gel time data (with 0.25% quaternary phosphonium accelerators).

DISCUSSION

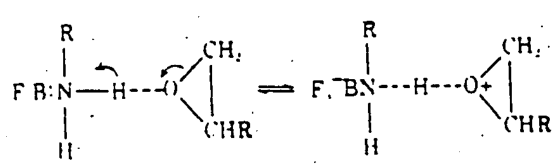
The reaction mechanism which makes these quaternary phosphonium compounds such effective accelerators for anhydride-cured epoxy resins is not clear at this time. The most obvious mechanism would be one whereby the quaternary phosphonium salts would dissociate into free phosphine (and possibly alkyl halide or acid) in heating. This type of mechanism has been attributed to the accelerator properties of quaternary ammonium compounds[14]:

$$R_4P^+X^- \rightleftharpoons R_3P + RX$$

$$\Updownarrow$$

$$HX \text{ (acid)} + R \text{ (olefin)}$$

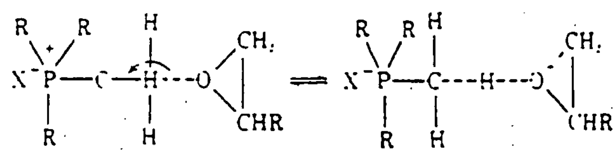
The free phosphine, being basic, would then be available to react with both the epoxy resin and the anhydride. However, thermal stability data on these quaternary phosphonium salts[15,16] indicate that they can be stable above 200°C so that such a dissociation mechanism seems unlikely. Recent work on the curing mechanism between amine–Lewis acids adducts and epoxy resins[17] seems to point to a mechanism in which little or no dissociation of the amine adduct occurs during cure. It has been proposed that in these systems a complex between the amine–Lewis acid adduct and epoxy occurs, e.g., with BF_3:MEA and epoxy, the following complex is formed:



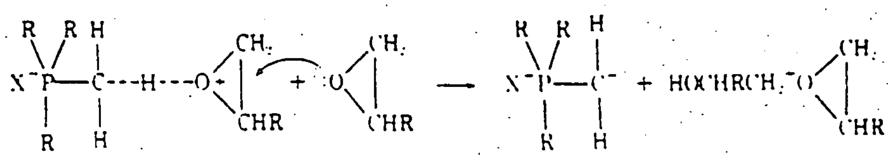
There is then a competition between the two bases, the epoxy ring and the amine,

for the hydrogen atom. Since the amine is more basic, the hydrogen will normally be more strongly bonded to the nitrogen than to the oxygen. However, since the oxygen atom is contributing a portion of its electrons to the amine hydrogen atom, it will acquire a partial positive charge thereby causing a partial shift of electrons from an adjacent carbon atom as shown above. The curing mechanism at elevated temperature is then thought to proceed through an initiation mechanism resulting from the attack of nucleophile (such as an epoxy oxygen) on this complex to form oxonium ions, which are the propagating species in the subsequent polymerization.

A similar mechanism may take place in the accelerated polymerization of anhydride-cured epoxy resins with quaternary phosphonium compounds. In the case of a methyltrialkyl-type phosphonium salt, such as MTOP-DMP, the methyl (CH_3) group attached to the phosphine phosphorus atom (P) would be expected to be fairly acidic in character (because of the close proximity of the empty d-orbitals of the phosphorus atom), and the acidic protons would be available for bonding with nucleophiles such as an epoxy oxygen. Thus,

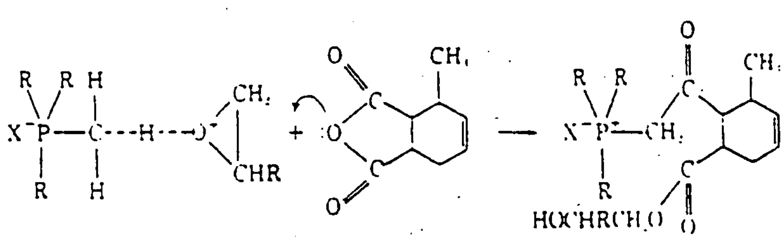


Although the quaternary phosphonium salt is written above as being ionic, it is now generally accepted that quaternary phosphonium compounds are more covalent in character than analogous quaternary ammonium compounds[18] (because of the close proximity of empty $3d$ electron orbits in the phosphorus atom). The epoxy–phosphonium salt adduct would then be vulnerable to attack by another epoxy molecule resulting in the formation of an oxonium ion:



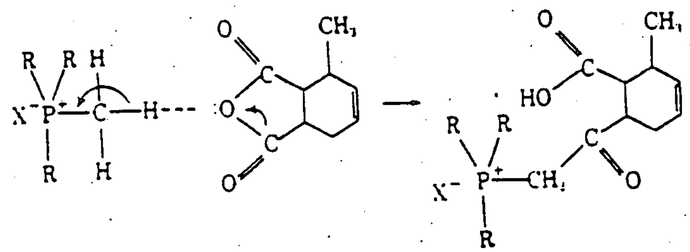
Mechanism I

During this reaction step, the electronic structure of the phosphorus atom will change from a sp^3d trigonal bipyramidal hybridization to a configuration closer to an octahedral sp^3d^2 atom. It is a well known fact that phosphorus compounds, because of the presence of empty d-orbitals, can take up this octahedral configuration.[19] Also, reaction of this epoxy–phosphonium salt adduct with 1-methyltetrahydrophthalic anhydride is likely to form active hydroxy compounds:



Mechanism II

Direct reaction between the anhydride and quaternary phosphonium salt, however, is also a possibility:



Mechanism III

After the formation of carboxyl groups, direct epoxy–carboxylic acid reaction leading to polymerization will occur. All of these initiation reactions result in the formation of "active hydrogen" either in the form of carboxyl or hydroxyl groups. Once this occurs, then a normal epoxy–anhydride-type polymerization will proceed.[20] The homopolymerization of epoxy catalyzed by quaternary phosphonium salt (i.e., mechanism I) would probably proceed at a fairly sluggish pace but might become more significant at higher temperatures and at higher accelerator concentrations.[21] In the case of the tetraalkylphosphonium salts such as TBPA, the "active" hydrogen, which is removed by reaction with a nucleophile, is most likely to come from the β-carbon atom on the alkyl chain adjacent to the phosphorus atom. However, TBPA may be a special case since it contains one molecule of acetic acid per molecule of phosphonium salt as "water" of crystallization from its purification procedure. The role of the acetic acid may well be to supply "active" hydrogen to anhydride and epoxy.

The low activation energy value (i.e., 16.0 kcal/mole), computed from the data in Figure 6, would suggest that the rate-determining step in the initiation mechanism involves the dissociation of the phosphonium compound–epoxy or phosphonium compound–anhydride complexes to form the initiation species illustrated by mechanisms I, II, and III. This dissociation involves the breaking of a hydrogen bridge and the transfer of a proton to the epoxy or anhydride oxygen (i.e., the breaking of a low-energy bond occurs). Hydrogen bond strengths are known to vary anywhere from 8.0 up to 30.0 kcal/mole.

In this discussion the assumption has been made that the phosphonium compounds play a role only in the initiation mechanism and do not contribute significantly to the propagation rates. Although this might be true for low concentrations of phosphonium compound, it may not hold for higher values. The deviations from linearity noted in the Arrhenius plot shown in Figure 7 for the epoxy–anhydride resin with higher accelerator concentrations (0.25%) may be a consequence of the phosphonium compounds playing a significant role in the propagation rates (i.e., the phosphonium compounds are involved directly in the formation of crosslinks). However, in such a complex system as this, other explanations are also possible for these observed deviations.

To illustrate the effectiveness of these quaternary phosphonium salts as accelerators for anhydride-cured epoxy resins, a comparison of MTOP-DMP and TBPA with other well-known accelerators is given in Table III. The data were obtained from work done in this laboratory using the same resin system. To

TABLE III
Relative Reactivities of Different Accelerators with Epoxy-Anhydride Resin at 150° and 135°C

Accelerator added to resin	Concentration in epoxy-anhydride resin: phr on resin	Concentration in epoxy-anhydride resin: Moles × 10^{-4} in 200 g resin	Gel time at 150°C, min	Gel time at 135°C, min	Relative reactivities of accelerators (R) × 10^{-4} min moles[a]: 150°C	Relative reactivities of accelerators (R) × 10^{-4} min moles[a]: 135°C
MTOP-DMP (MW 510.7)	0.020	0.78	90	—	70.2	—
	0.060	2.34	—	80	—	187.3
TBPA (MW 378.4)	0.020	1.06	65	—	68.8	—
	0.060	3.18	—	60	—	190.1
Benzyltriethylammonium chloride (MW 227.8)	0.020	1.77	50	—	88.5	—
Benzyltrimethylammonium iodide (MW 277.2)	0.020	1.45	40	—	58.0	—
	0.100	7.22	12	30	86.6	216.0
1-Methylimidazole (MW 82.1)	0.063	15.22	12	23	183.0	350.0
2-Methylimidazole (MW 82.1)	0.063	15.22	—	17	—	259.0
Zinc stearate (MW 631.4)	4.500	79.20	—	40	—	3165.0
Zinc oleate (MW 627.4)	2.500	79.80	—	20	—	1592.0
N,N Diethylethanolamine (MW 117.2)	0.025	4.27	50	—	—	213.5
Uranyl nitrate [$UO_2(NO_3)_2 \cdot 6H_2O$] (MW 502.1)	0.020	0.80	20	—	16.0	—

[a] The quantity R is given by product of (gel time) × (accelerator concentration, in moles in 200 g resin).

make the comparison valid, the concentration given for each of these materials has been converted from "phr" to "moles/200 g resin." Thus, the comparison is made on a molecular concentration basis instead of weight. Gel times were recorded at 135° and 150°C as shown in Table III, and the measure of relative reactivity (R) of each of the accelerators is given by the expression

$$R = (\text{time to reach gel point, in min}) \times (\text{molar concentration of accelerator, in moles/200 mg resin})$$

Two sets of data have thus been calculated at 135° and 150°C and resolved: the *more reactive* the accelerator, the *lower* the product R will be.

Comparison of these data show quite clearly how much more reactive the phosphonium salts are in the resin system than compounds such as substituted imidazoles and organozinc salts (e.g., zinc stearate and octoate). The only accelerator that shows substantially more potency than the quaternary phosphonium salts is uranyl nitrate. However, this compound is not a latent accelerator in the sense that storage lifetimes are only of the order of a few days.

References

1. I. N. Elbling and A. B. Finestone, Ger. Pat. 1,162,439 (to Westinghouse) (Nov. 1958).
2. L. F. Betnamont, Br. Pat. 869,969 (to Shell) (June 1961).
3. W. R. Proops and G. W. Fowler, Br. Pat. 966,917 (to Union Carbide) (Feb. 1965).
4. A. J. Landua, *ACS Div. Org. Coatings Plast. Chem. Prepr.*, 24 (2), 299 (Sept. 1964).
5. R. B. Feuchtbaum, *Insulation*, p. 47. (Sept. 1962).
6. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 5, p. 20.
7. W. J. Belanger, U.S. Pat. 2,928,807 (to Devoe and Raynolds Co.) (March 1960).
8. D. A. Rogers, Jr., and R. N. Kauffman, Westinghouse R&D unpublished work.
9. H. L. Vincent, C. L. Frye, and P. E. Oppliger, *Adv. Chem. Ser.*, 92, 164 (1970).
10. S. H. Langer and I. N. Elbling, *Ind. Eng. Chem.*, 49, 1113 (1957).
11. S. H. Langer, I. N. Elbling, A. B. Finestone, and W. R. Thomas, *J. Appl. Polym. Sci.*, 5, 370 (1961).
12. Belg. Pat. 633,330 (to CIBA) (1963).
13. J. D. B. Smith, U.S. Pat. 3,784,583 (to Westinghouse) (Jan. 1974).
14. Reference 6, Chap. 9, p. 5
15. D. A. Rogers and J. D. B. Smith, U.S. Pat. 3,759,866 (to Westinghouse) (Sept. 1973).
16. C. K. Ingold, G. F. Fenton, L. Hey, and C. K. Ingold, *J. Chem. Soc.*, 989 (1933).
17. J. J. Harris and S. C. Temin, *J. Appl. Polym. Sci.*, 10, 523 (1966).
18. G. M. Kosolapoff, *Organophosphorous Compounds*, Wiley, New York, 1950, Chap. 5, p. 78.
19. R. B. Heslop and P. L. Robinson, *Inorganic Chemistry*, Elsevier, Amsterdam–New York, 1960, Chap. 20, pp. 310–313.
20. Reference 6, Chap. 5, pp. 20–24.
21. J. D. B. Smith, Westinghouse R&D unpublished data.

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